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Final Technical Report

on

MATERIALS STUDIES FOR SOLAR CELL STRUCTURES

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INTRODUCTION

The purpose of this research program was the study of possible techniques of measurement and reduction of the surface recombination losses in solar cell structures. The primary material to be investigated was InP. Samples of epitaxial InP were grown for subsequent examination and chemical surface treatment. The surface investigations employed relative photoluminescence intensity (PLI) measurements. The surface emission or transmitted PLI techniques were similar to those described by Mettler [1] and Jenkins, et al. [2].

Surface recombination rates are controlled by the density of surface states with respect to energy and the position of the Fermi level at the surface. Various surface treatments may affect either of those two factors controlling the recombination rate. For a radiative recombination process, excess carriers may be lost nonradiatively at the surface states. The principle of the PLI measurement techniques of References [1] and [2] is the variation of the depth of excitation of the excess electron-hole pairs by varying the wavelength of the optical excitation source.

SURFACE RECOMBINATION STUDIES IN InP

Epitaxial Layer Preparation

Approximately 5 μm thick layers of manganese and zinc doped p-type InP were grown by liquid phase electroepitaxy (LPEE) on (100)-oriented InP substrates [3]. The surfaces of the LPEE-grown material contained microscopic pits and striations as a result of the growth process, and thus the material quality may vary over the area of the 7x7 mm substrates. The Hall measurement carrier concentrations in the 5 μm layers were in the 10^{17}-10^{18} cm^{-3} range for growths on semi-insulating InP substrates.

Photoluminescence Measurement System

The photoluminescence intensity of the epitaxial samples was determined at room temperature using an 2-watt argon ion laser as an excitation source at 514 or 488 nm. For spectral measurements the photoluminescence (PL) emission was collected with a lens and focussed onto the entrance slit of a 0.5-meter diffraction grating spectrometer. Also coupled into the optical system was a 35 mW He-Ne laser providing a more deeply penetrating excitation at 632 nm. A laser power controller was inserted in the He-Ne beam to stabilize the

intensity at the sample, while the argon ion laser had an internal light intensity stabilizer. Typically, the output powers were 25 mW for the He-Ne and 40 mW for the argon ion laser.

A unique configuration of the optical system was the chopping of the two laser beams at different frequencies (c. 227 and 277 Hz). The electrical output of the spectrometer photomultiplier detector was coupled to two lock-in amplifiers referenced to the two chopping frequencies. A computer-based data acquisition system sampled the wavelength and lock-in amplifier output information. These data could then be manipulated later for analysis.

In the dual-wavelength excitation mode of PLI measurements the two laser beams were aligned to the same point on the sample surface in order to collect the emitted PL radiation with the spectrometer collection lens. The sample normal was aligned with the spectrometer entrance slit, while the He-Ne laser beam was incident at $28°$ with respect to the normal and the Ar laser beam at $41°$. The absorption depths in InP for the Ar 488 nm and He-Ne 632 nm wavelengths are approximately 0.07 μm and 0.16 μm, respectively. Thus, this combination of laser excitation produces about a 2:1 difference in the depth of the excess hole-electron generation volume with respect to the incident sample surface.

An alternative mode of photoluminescence investigation was the transmitted PLI detection system consisted of a laser beam chopper, Si photovoltaic detector, a current amplifier, and a lock-in amplifier. In this method sample was mounted on an aperture plate over the detector which sensed the spectrally integrated transmitted PLI. Laser line optical bandpass filters were used to eliminate extraneous long wavelength emission from the argon laser. The measurement of the integrated transmitted PLI could also be performed in a DC mode with an unchopped laser beam excitation. Conceivably, the transmitted PLI could be spectrally scanned with the single or dual wavelength excitation procedure by mounting the sample in the optical collection path of the spectrometer.

Surface Treatments

One of the wet chemical surface treatments tried was that reported by Jenkins, *et al.* utilizing 15% HF in deionized water [2]. After soaking for 30 minutes in this solution, the 514 nm-excited transmitted PLI was observed to increase by perhaps a factor of 2 with respect to the as-grown epilayer surface. Also, as observed by Jenkins, *et al.* this PLI decayed with continued exposure to the Ar ion laser beam. Another chemical treatment used to decrease the

surface recombination velocity in GaAs is the appLication of an aqueous $Na_2S \cdot 9H_2O$ solution [4,5]. The sulfide was prepared here in a 1.0 M concentration, dropped on the InP surface and spun at 5000 RPM to create a thin layer as the solution dried. Visually, this film was very nonuniform with striations, and the transmitted PLI was decreased considerably with respect to the surface before treatment. It is not known whether the PLI reduction is due to attenuation losses in the deposited surface layer or to an increase in the surface recombination velocity. As was indicated above, the available epitaxially-grown InP layers exhibited were very nonuniform in surface morphology, which was observed by large variations in PLI over the surface area. Thus, the result of the procedure of performing a surface measurement on an area of a few square millimeters, then chemically treating the surface and remeasuring the PLI is strongly dependent upon the realignment of the sample in the optical system.

Results of Spectral PLI Measurements

The two lock-in amplifier output voltages were recorded during a single wavelength scan. Thus, any alterations in the surface state conditions which occurred due to the laser excitation were simultaneously affecting the short and long wavelength emission spectra. The spectral results are presented by normalizing the voltage data with respect to their peak amplitude in the scan (V_{Am}, V_{HNn}). The ratio of the normalized argon laser spectrum (at 488 or 514 nm) to the He-Ne laser spectrum is also calculated (V_{Am}/V_{HNn}). This presentation ignores any nonlinear dependence of the PLI spectra upon the excitation power density. While no theoretical explanation of the spectral PLI shapes is offered here, it is felt that the developments presented in References [1] and [2] can be utilized in the analysis of the data. The limited quantity and variable surface quality of the epitaxial InP layers precluded an investigation of the surface treatment effects. Some example PLI spectra are presented here.

In Fig. 1 the tails of the normalized He-Ne spectrum exceed the 488 nm Ar spectrum for the Mn-doped InP-A4 sample. The V_{Am}/V_{HNn} ratio is less than unity over most of the 8900-9400 Å range. This sample surface had been exposed to air for six months. The spectra for the air-exposed Zn-doped InP-B3 sample are shown in Fig. 2. The ratio spectrum differs from the InP-A4 sample surface by exhibiting a greater than unity value on the long wavelength side of the PL peak. This sample InP-B3 was soaked in a 10% HF in H_2O solution for one minute. Fig. 3 demonstrates an alteration of the relation between the 488 and 632 nm spectra. The peak

PL voltage levels were reduced to about 60% of the presoak values. This reduction in PLI with HF treatment is contrary to the observations after longer soak times here and in Ref. [2]. Another example of the ratioed spectra is shown in Fig. 4 for a liquid phase epitaxially grown layer of $Ga_xAl_{1-x}As$ on GaAs In this case the voltage ratio V_{Arn}/V_{HNn} exceeds unity over most of the spectral range.

CONCLUSION

A dual-wavelength excitation and measurement technique for photoluminescence intensity analysis has been described. This data presentation technique should be useful for comparing the surface characteristics of different samples or treatments, as inferred from the spectral PLI behavior.
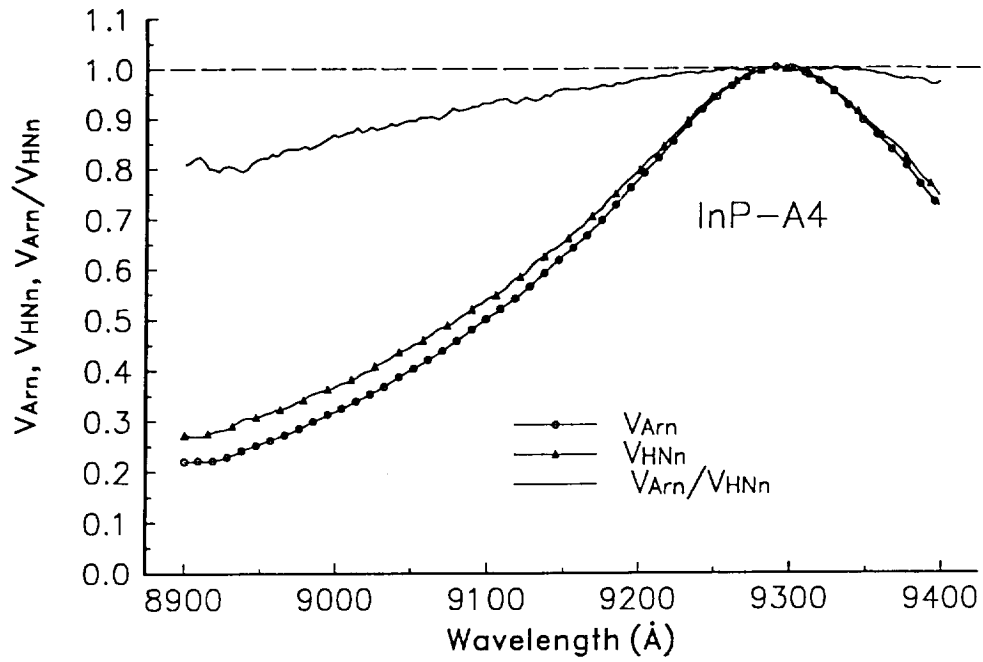
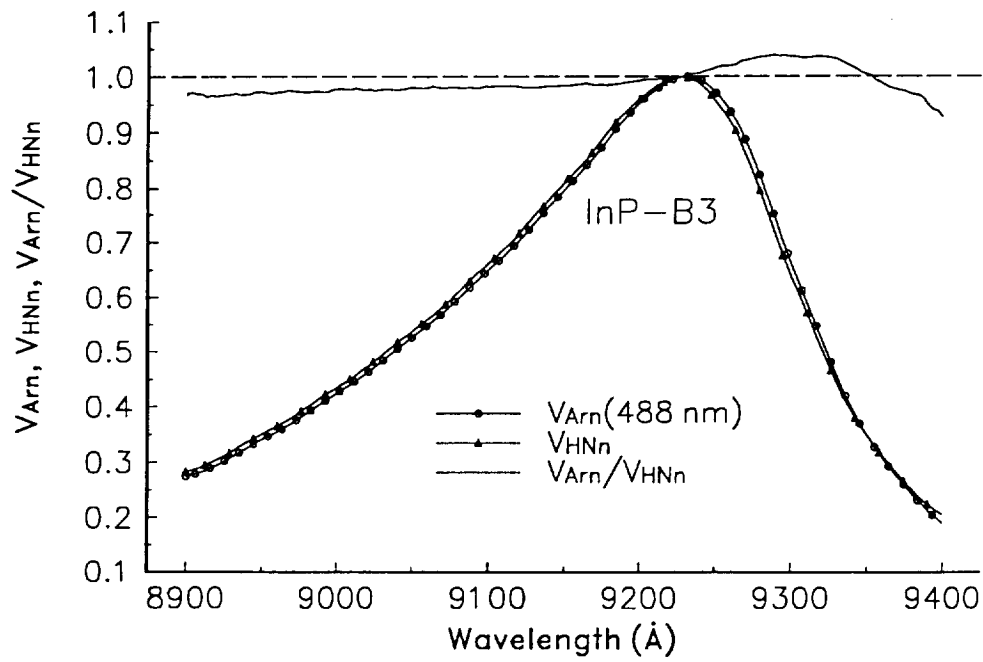Fig. 1. Dual-wavelength excitation voltage spectra for epitaxial sample InP-A4.

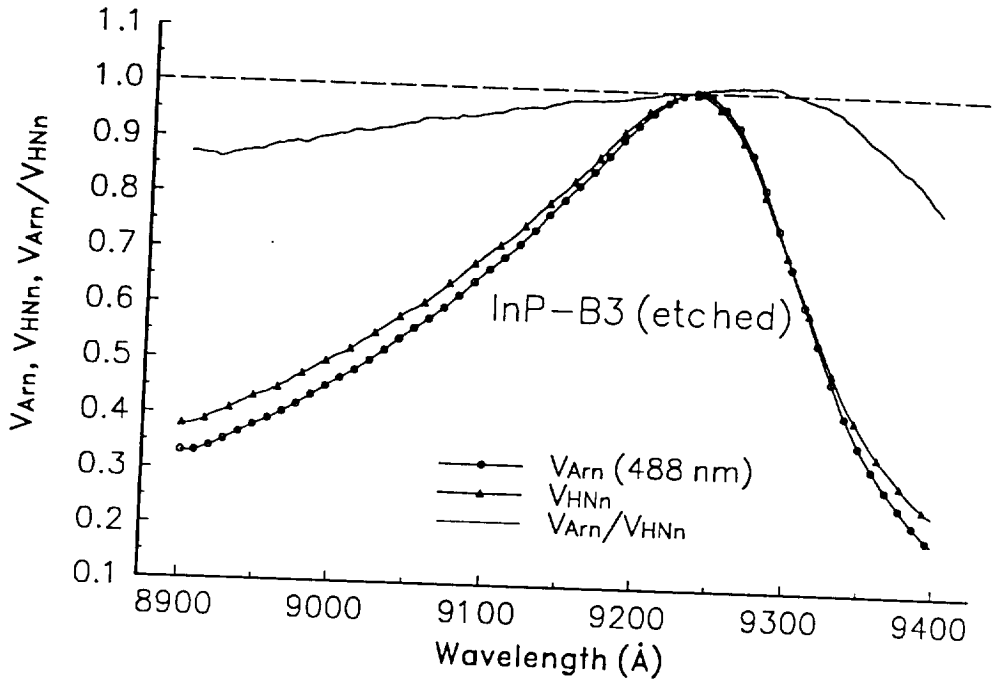Fig. 2. Dual-wavelength excitation voltage spectra for epitaxial sample InP-B3.

Fig. 3. Dual-wavelength excitation voltage spectra for epitaxial sample InP-B3 after soaking in dilute HF solution.
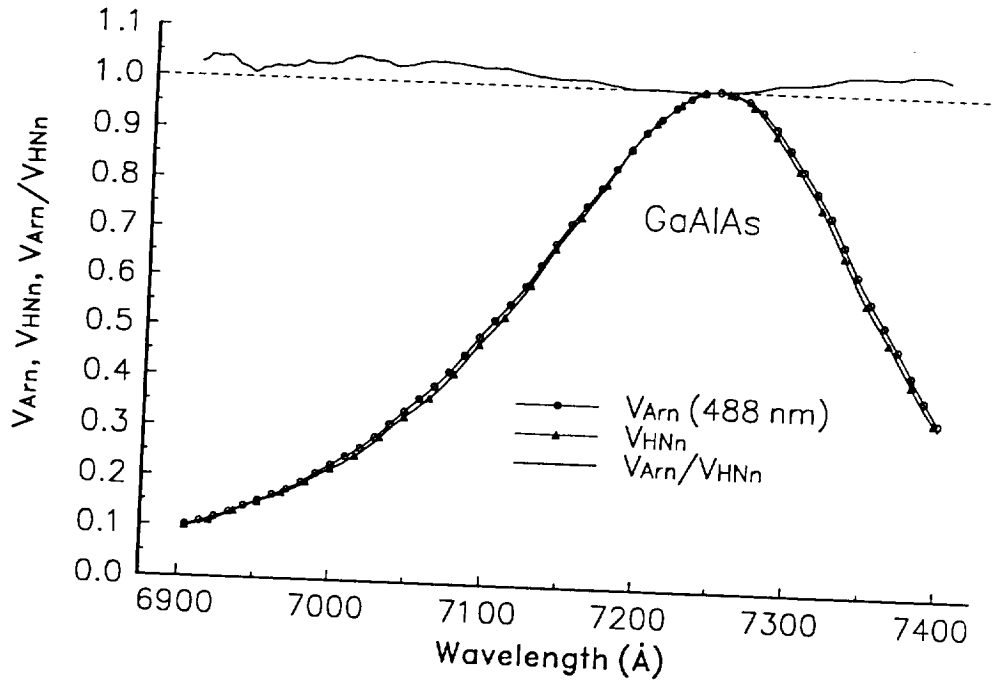

Fig. 4. Dual-wavelength excitation voltage spectra for an epitaxial GaAlAs sample.

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